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Molecular force field of sulphadimethoxine

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Abstract Infrared and Raman spectroscopic study of the broad spectrum antibiotic sulpha drug sulphadimethoxine have been made. Based on the assignments made to various vibrational frequencies, force constants are evaluated. Force constant studies are needed to have a qualitative study on the properties of molecules. In the present paper, the molecular model, the force constants and G matrices used for the molecule and the method of evaluation of force constants are given. The normal coordinate analysis is attempted on the molecule, treating it as an SO_2XY type molecule.

Keywords Molecular force field, sulphadimethoxine, force constants

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Vibrational spectroscopic studies on multi-ring molecules are very meagrely available in literature. Due to the complexity, force constant studies on these molecules are still less. In this communication, we herewith present the force constants evaluated for the broad spectrum sulpha drug 4-*p*(-aminobenzene-sulphanomido-)-2,6-dimethoxy pyrimidine whose trade name is sulphadimethoxine. Knowledge of the various vibrational frequencies of the molecule is needed for this. The details of the assignments of various vibrational modes made by us are given elsewhere [1]. In this communication, we report the force constants evaluated for the molecule. Using the force constants obtained by iteration method, vibrational frequencies are calculated and the agreement between calculated and observed frequencies is satisfactory.

In many of the sulpha drug molecules, there is a common group -SO_2 NH-substituted with para-amino benzene on one side and a characteristic group of these drugs on the other side. The SO_2NH group is mainly responsible for the biological activity of the sulpha drug [1,2]. The substituent groups present on either side of the SO_2NH group change the percentage activity.

The substituent groups are taken as point masses and the sulpha drug molecule is treated as SO_2XY type molecule for the purpose of calculating the force field. The stretching, bending and interaction force constants are evaluated for the sulpha drug molecules. The results are compared with those relevant values quoted in literature for the SO_2XY

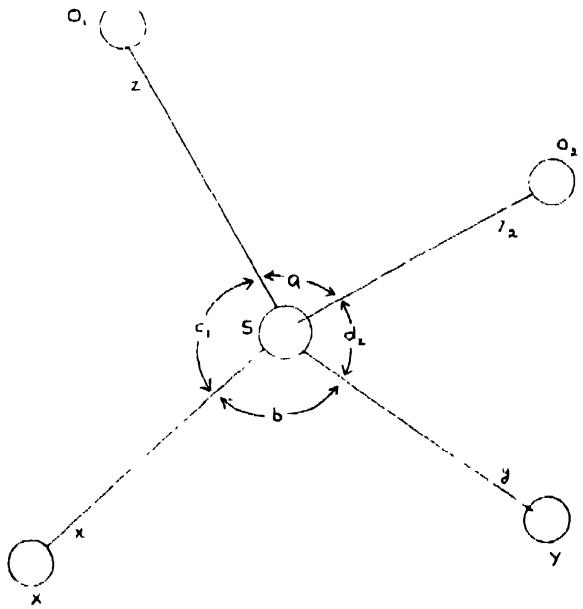

Figure 1. Geometry of SO_2XY type molecule

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type molecules. The geometry of the molecule is shown in Figure 1. C_s symmetry is assumed for the SO_2XY type molecules [3 5]. With C_s symmetry, the SO_2XY type molecule gives rise to six a' type and three a'' type vibrations, both being non-degenerate and Infrared and Raman active.

Following the Wilson's procedure [5], the internal displacement coordinates selected are .

1) The changes in the three bond distances viz., z(S–O), x(S–X) and y(S–Y); and

2) The changes in the six interbond angles, viz., a(O1–S–O2), b(X–S–Y), $c1$(X–S–O1), $c2$(X–S–O2), $d1$(O1–S–Y) and $d2$(O2–S–Y)

The following internal symmetry coordinates are taken as the sufficient coordinates to solve the problem.

$S1 = \Delta x$, $S2 = \Delta y$; $S3 = k1(\Delta z1 + \Delta z2)$,

$S4 = k2(\Delta a - \Delta c1 - \Delta c2 + \Delta d1 + \Delta d2 - \Delta b)$;

$S5 = k2(\Delta d1 + \Delta d2 - 2\Delta a)$, $S6 = k2(\Delta c1 + \Delta c2 - 2\Delta b)$;

$S' = k2(\Delta a + \Delta c1 + \Delta c2 + \Delta d1 + \Delta d2 + \Delta b) = 0$ (redundant coordinate),

$S7 = k1(\Delta c1 - \Delta c2)$, $S8 = k1(\Delta z1 - \Delta z2)$;

$S9 = k1(\Delta d1 - \Delta d2)$,

The transformation matrix U for both species a' and a'' can be formed very easily from the coordinates $S1$ to $S9$. Using the U-matrix, symmetrized F and G-matrices are formed for a' and a'' species.

The symmetrized elements of the F-matrix are

$F_{11} = f_x$, $F_{12} = f_{xy}$, $F_{13} = k7\, f_{xz}$,

$F_{14} = -k2(f_{xb} + 2f_{xc})$; $F_{15} = 0$;

$F_{16} = k3(f_{xc} - f_{xb})$, $F_{22} = f_y$; $F_{23} = k7\, f_{yz}$;

$F_{24} = k2(2f_{xd} - f_{yb})$, $F_{25} = k3\, f_{yd}$,

$F_{26} = -k3\, f_{yb}$; $F_{33} = f_z + f_{zz}$;

$F_{34} = k4(f_{za} + f_{zd} + f_{zd'} - f_{zc} - f_{zc'})$;

$F_{35} = k4(f_{zd} + f_{zd'} - 2f_{za})$;

$F36 = k4(f_{zc} + f_{zc'})$, $F44 = k5(2f_d + 2f_c + f_a + f_b)$;

$F45 = k6(f_d - f_a)$; $F46 = k6(f_b - f_c)$; $F55 = k6(2f_a + f_d)$;

$F56 = 0$; $F66 = k6(2f_b + f_c)$,

where $k1 = 2^{(-1/2)}$, $k2 = 6^{(-1/2)}$, $k3 = (2/3)^{(1/2)}$,

$k4 = 3^{(-1/2)}$, $k5 = 6^{(-1)}$, $k6 = 3^{(-1)}$, $k7 = 2^{(1/2)}$.

The symmetrized G-matrix elements for both species are transferred from the earlier works [7,8] The bond distances used for S–O, C–S and S–N are 1.446, 1.74 and 1.65 Å respectively [9]. The mass of Y-group is taken as 124.154 a.m.u. and the mass of the X-group as 92.122 a.m.u.

Using the bond distances, masses of atoms and bond angles, the values of G-Matrix elements for a' and a'' species are calculated. The calculated values of a' species G-matrix elements of SO_2XY type molecules are

$G11 = 0.04313$, $G12 = -0.01076$, $G13 = -0.01522$,
$G14 = 0.04942$, $G15 = -0.00106$, $G16 = -0.00212$,
$G22 = 0.03876$, $G23 = -0.01522$, $G24 = -0.01718$,
$G25 = -0.03437$, $G26 = 0.03001$, $G33 = 0.08402$,
$G34 = -0.02280$, $G35 = 0.02505$, $G36 = -0.01972$,
$G44 = 0.11714$, $G45 = -0.0097$, $G46 = -0.02232$,
$G55 = 0.11232$, $G56 = -0.02938$, $G66 = 0.047$.

Similarly, the a'' symmetrized G-matrix elements and their calculated values are :

$G11 = 0.06666$, $G12 = -0.03676$, $G13 = 0.01767$,
$G22 = 0.10554$, $G23 = -0.03819$, $G33 = 0.06735$.

The force constants are evaluated by solving the secular equation $|GF - \lambda E| = 0$. The initial values of the force constants needed to solve the problem are taken from literature and they are altered by an iterative method to fix the force field of the molecule until they reproduced the observed frequencies.

The calculated values of a' species F-matrix elements of SO_2XY type molecule from the relations given are :

$F11 = 4.103$, $F12 = 0.879$, $F13 = 0.3026$, $F22 = 6.364$,
$F23 = 0.676$,
$F33 = 9.3206$ (all values in mdynes/Å),
$F14 = -0.3319$, $F15 = 0$, $F16 = 0.3267$, $F24 = -0.7034$,
$F25 = -0.6507$,
$F26 = -0.1053$, $F34 = -1.5744$, $F35 = -0.8008$,
$F36 = -1.0052$ (all values in mdynes/rad),
$F44 = 1.0525$, $F45 = 0.2347$, $F46 = -0.2203$,
$F55 = 0.9187$, $F56 = 0$,
$F66 = 0.7313$ (all values in mdynes.Å/rad^2).

The relationships between symmetrized force constants F and force constants f of a'' species are given by :

$F77 = f_z - f_{zz}$; $F78 = f_{zd} - f_{zd'}$; $F79 = f_{zc} - f_{zc'}$; $F88 = f_d$,
$F89 = 0$; $F99 = f_c$.

The calculated values of a'' species F-matrix elements of SO_2XY type molecule are :

$F11 = 12.9166$ (mdynes/Å),
$F12 = 0.079$, $F13 = 2.57$ (all values in mdynes/rad),
$F22 = 1.388$, $F23 = 0$; $F33 = 1.172$ (all values in mdynes.Å/rad^2).

Taking six force constants as starting set, many other force constants are evaluated and no reports are available on these in literature. The assignment of the observed frequencies of the X(C)-SO_2-Y(N) group are consistent with the results of this normal coordinate treatment.

There is an ambiguity in literature in the assignment of S–N stretching frequency and our calculations confirm that the assignment of 840 cm^{-1} is appropriate of S–N stretching. In addition to this, it is also possible to distinguish the SO_2 twisting and wagging modes of vibration relative to the

given internal symmetry coordinates. By this, it is possible to assign the vibrational frequencies to all the nine vibrational modes of $X-SO_2-Y$ group as given in Table 1.

Table 1. Comparison of calculated frequencies (cm^{-1}) with the observed frequencies of SO_2XY group on the sulpha drug molecules

Type of vibration	Calculated frequency	Observed frequency
a' species		
ν_1 S–X stretching	725	725
ν_2 S–Y(N) stretching	830	830
ν_3 S–O sym stretching	1150	1150
ν_4 SO_2 scissoring	545	545
ν_5 X(C)–S Y(N) bending	200	200
ν_6 SO_2 rocking	335	335
a'' species		
ν_7 SO_2 twisting	250	250
ν_8 S–O asym stretching	1310	1309.2
ν_9 SO_2 wagging	440	440

sym → symmetric, asym. → asymmetric

Since a large number of force constants have to be determined for which no earlier reported values are available in literature, the bend-bend interaction force constants and stretch-bend interaction force constants are neglected, as they are assumed to have a very little contribution. Also the simplifying assumption that interaction between like bonds are equal *e.g.* $x_1 = x_2$ is made.

A total of twenty *f*-matrix elements are calculated for sulphadimethoxine. Of these, three are stretching force constants, four are bending force constants, four bond stretching-stretching interaction constants and nine bond stretching-bending interaction force constants. The stretching and bending force constants are given in Table 2 and the interaction force constants are given in Table 3. For comparison, the calculated fundamental frequencies are given along with the observed ones in Table 1.

Table 2. Calculated values of force constants

Type of force constant	Value
Stretching force constants (md/Å)	
f_r. S–X(C)	4.103
f_R. S–O	11.1186
f_r. S–Y(N)	6.364
Bending force constants (md.Å/rad^2)	
f_α. O–S–O	0.684
f_γ. X(C)–S–O	1.172
f_β. O–S–Y(N)	1.388
f_δ. X(C)–S–Y(N)	0.511

Table 3. Interaction force constants for SO_2XY group in the sulpha drug molecules.

Type of interaction force constant	Value
Bond stretching-stretching (md/Å)	
$f_{rr'}$. S–X(C), S–O	0.428
$f_{rr'}$. S–Y(N), S–O	0.478
$f_{rr'}$. S–X(C), S–Y(N)	0.879
$f_{RR'}$. S–O, S–O	–1.798
Bond stretching-angle bending (md/rad)	
$f_{r\alpha}$. S–X(C), X(C)–S–O	0.348
$f_{r\beta}$. S–X(C), X(C)–S–Y(N)	0.117
$f_{q\alpha}$. S–Y(N), Y(N)–S–O	–0.797
$f_{q\beta}$. S–Y(N), X(N)–S–Y(N)	0.129
$f_{R\alpha}$. S–O, X(C)–S–O	0.258
$f_{R\gamma}$. S–O, X(C)–S–O′	–1.999
$f_{R\beta}$. S–O, Y(N)–S–O	0.137
$f_{R\beta'}$. S–O, Y(N)–S–O′	0.058
$f_{\alpha\alpha'}$. S–O, O–S–O	0.791

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